

Supplementary Information

Salting-in species induced self-assembly of stable MOFs

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S1. Chemicals and Materials

Zirconyl chloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$), **cerium(IV) ammonium nitrate** ($(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$) and **sodium thiocyanate** (NaSCN) were purchased from Shanghai Macklin Biochemical Co., Ltd.. **Sodium perchlorate monohydrate** ($\text{NaClO}_4 \cdot \text{H}_2\text{O}$), **chromic nitrate nonahydrate** ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and **aluminium chloride hexahydrate** ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$), **acetic acid (AA)** were purchased from Sipharm Chemical Reagent Co., Ltd.. **Sodium iodide (NaI)**, **2-nitroterephthalic acid (BDC-NO₂)**, **2-bromoterephthalic acid** and **2-methylterephthalic acid** were supplied by Shanghai D&B Biological Science and Technology Co., Ltd.. **2-aminoterephthalic acid (BDC-NH₂)** was supplied by Alfa Aesar Chemicals. Others were obtained from Shanghai Titan Scientific Co., Ltd.. All reagents were of analytical grade, and used without further purification. The applied water ($18.1 \text{ M}\Omega \cdot \text{cm}^{-1}$) in the experiments was purified from a NW Ultrapure Water System (Heal Force, China).

S2. Instruments and Methods

The powder X-ray diffraction (XRD) patterns were obtained on a Bruker D8 instrument using Cu K α radiation (40 kV, 40 mA). Transmission electron microscopy (TEM) was conducted on a JEM-2100F electron microscope. Scanning electron microscopy (SEM) was performed with a Hitachi S-4800 electron microscope. **N₂ sorption isotherms** were recorded using a surface area and pore size analyzer (Micromeritics Tristar 3020). All of the samples were degassed under vacuum at 120 °C for 12 h prior to analysis. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method using adsorption data at a relative pressure (P/P_0) lower than 0.15. UV-vis absorption spectra were measured with a UV-2550 spectrophotometer (Shimadzu, Tokyo, Japan). FTIR spectroscopy was conducted on a Nicolet 7000-C spectrometer with a resolution of 4 cm^{-1} using the KBr disc method. Thermogravimetric analysis (TGA) was recorded on a Perkin-Elmer thermogravimetric analyzer by heating the sample to 800 °C in air (50 mL min^{-1})

at a heating rate of 10 °C min⁻¹. ¹H nuclear magnetic resonance (¹H NMR) spectra were carried out with a Bruker Avance III 400.

S3. Solubility measurement

The solubilities of 1,4-dicarboxybenzene (BDC) and its derivatives in the presence of 0 - 2M salting-in or salting-out species were measured as following.

Stock solutions of the salting-in or salting-out species were prepared by mixing water and the pre-determined weight of various species, pH values were adjusted by hydrochloric acid and sodium hydroxide. Excess amount of ligands were transferred into test tubes to which 0.3 mL of water or the stock solution was added. The suspension was incubated at 25 °C for 24 h to reach equilibrium. Subsequently, the suspension was centrifuged at 25 °C and 13000 rpm for 35 min to obtain a supernatant saturated with the ligands. After appropriate dilution of the supernatant with water, the absorbance of the supernatant was determined spectrophotometrically at 240 nm for BDC, 329 nm for BDC-NH₂, 311 nm for BDC-OH, 243 nm for BDC-CH₃, 240 nm for BDC-Br, and 228 nm for BDC-NO₂ using a UV-vis spectrophotometer. The absorbance was converted to the concentration based on the standard curve determined for each ligand. Since NaI, NaNO₃, NaSCN and GdmCl have their own strong absorption peaks at 200-240 nm, which completely overlap with the absorption of BDC, we only studied their effects on the solubility of BDC-NH₂ and gave a qualitative result based on orthogonal experiments. The effects of NaClO₄, L-arginine and NaCl on the solubilities of all the applied ligands were measured.

UiO and MIL series MOFs are both synthesized under strong acidic conditions. Because BDC and its derivatives contain two carboxyl groups, their solubilities are pH dependent. So the effects of salting-in species on their solubility were measured at different pHs of 6.5 and 2.5. The solubility trend of ligands in the presence of additives at pH 2.5 is similar to that at

pH 6.5 which was measured and shown in the following Figures S1 and S2.

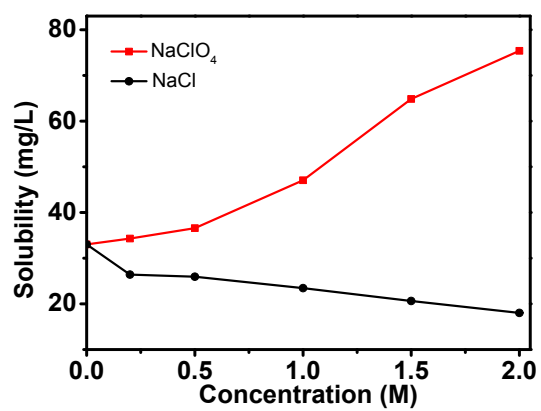


Figure S1. Solubility of BDC in the presence of salting-in species of NaClO₄ and salting-out species of NaCl as a function of their concentration at pH 6.5.

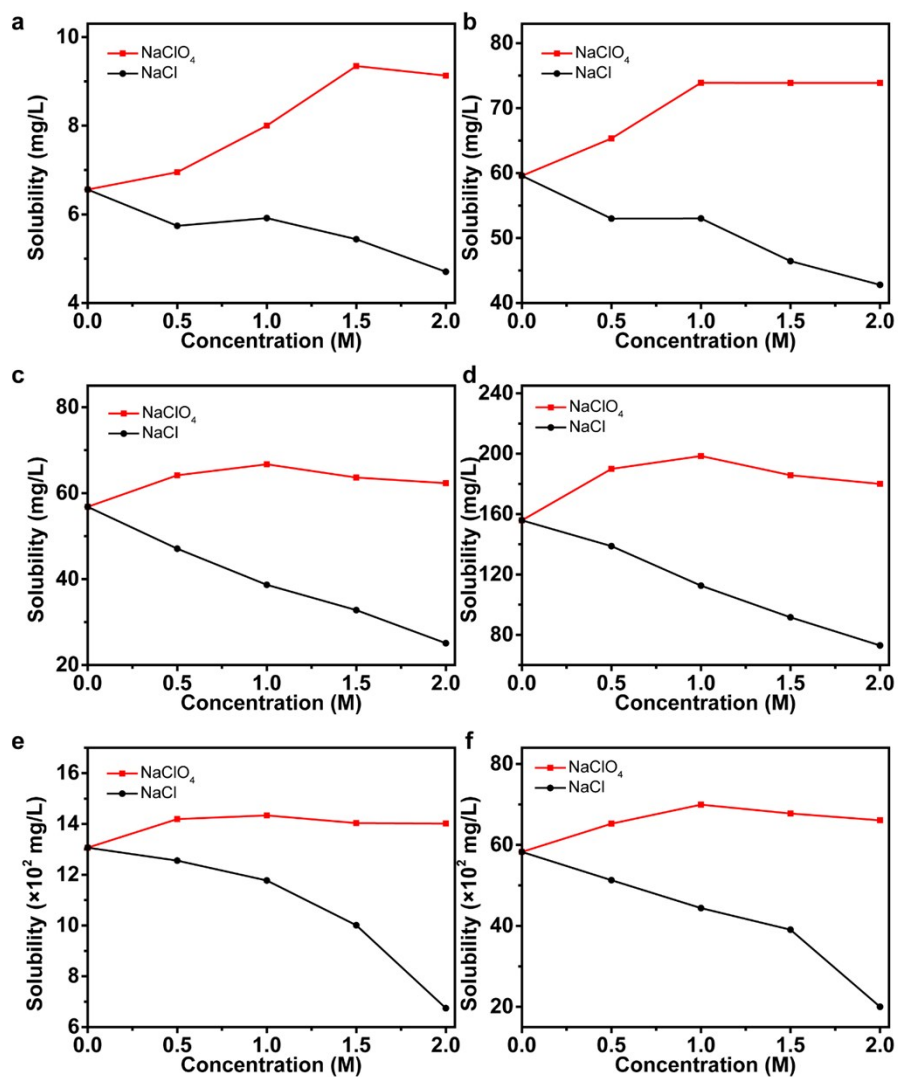


Figure S2. Solubility of BDC (a), BDC-NH₂ (b), BDC-OH (c), BDC-CH₃ (d), BDC-Br (e) and BDC-NO₂ (f) in the presence of salting-in species of NaClO₄ and salting-out species of NaCl as a function of their concentration at pH 2.5.

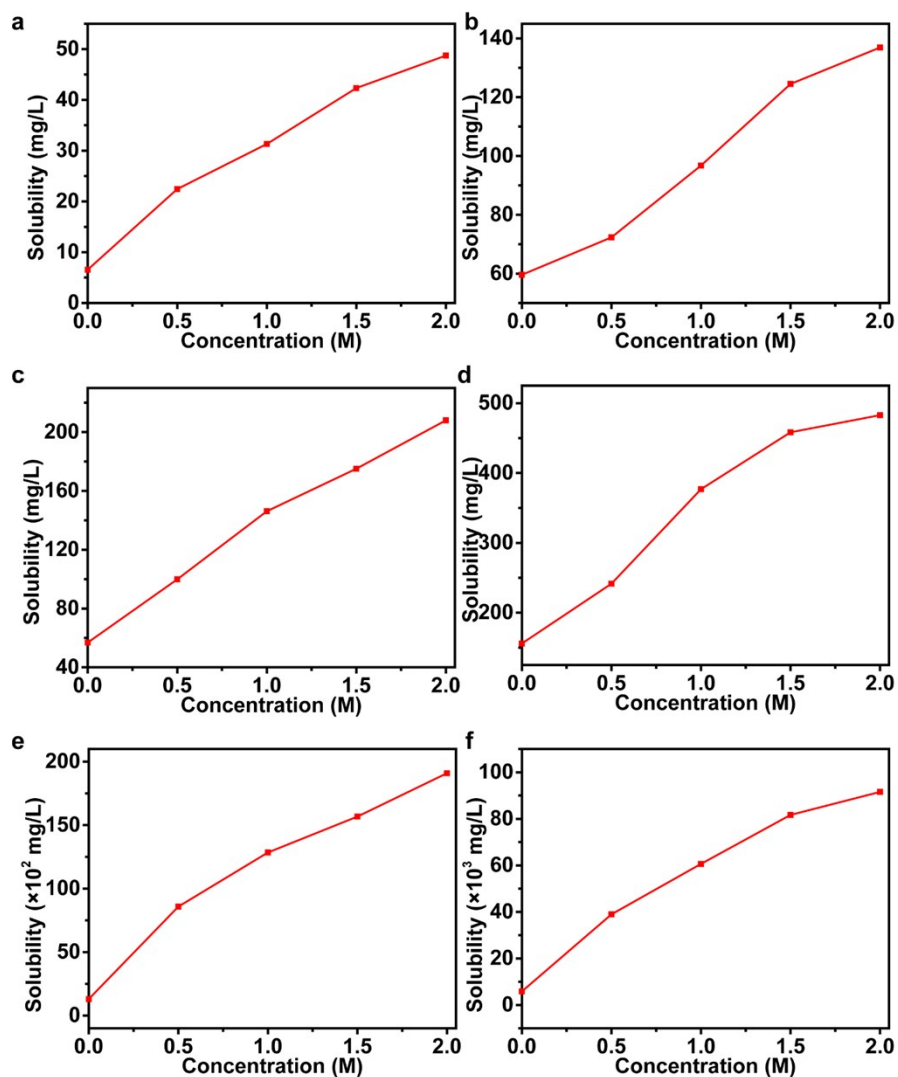


Figure S3. Solubilities of BDC (a), BDC-NH₂ (b), BDC-OH (c), BDC-CH₃ (d), BDC-Br (e) and BDC-NO₂ (f) in the presence of L-arginine as a function of L-arginine concentration at pH 2.5.

S4. Materials Synthesis

S4.1. Synthesis of hcp-UiO-66(Zr)-X

When NaNO₃, NaI, NaClO₄, NaSCN and GdmCl were used as the mediators, the molar composition of the reagents was 1ZrOCl₂·8H₂O: 0.75BDC: 3X: 17AA: 338H₂O, where X = NaNO₃, NaI, NaClO₄, NaSCN and GdmCl. To investigate the optimum synthesis conditions, the feed ratio of AA to Zr was varied from 0 to 24 and the feed ratio of NaI to Zr was varied from 0 to 6.

In a typical synthesis, the hcp-UiO-66-NaI was prepared as following.

NaI (450 mg, 3 mmol) was dissolved in 6 mL deionized water, and then AA (1 mL, 17 mmol) was added. The mixture was stirred to form a homogeneous solution. Subsequently, ZrOCl₂·8H₂O (322 mg, 1 mmol) and BDC (125 mg, 0.75 mmol) were added into the above mixture. Then, the mixture was heated to 90 °C for 24 h under static conditions. The resultant solid was isolated by centrifugation and washed with water for three times and ethanol twice. To remove the unreacted BDC, the as-synthesized sample was washed with DMF twice and soaked in methanol for three days at 60 °C, during which methanol was replaced daily. Finally, the product was dried overnight at 60 °C under vacuum.

S4.2. Synthesis of UiO-66(Zr)-Arg

L-arginine (1400 mg, 8mmol) was dissolved in 6 mL deionized water with 1 mL HCl (37%), ZrOCl₂·8H₂O (322 mg, 1 mmol) and BDC (166 mg, 1 mmol) were added into the above mixture. Then, the mixture was heated to 90 °C for 24 h under static condition. The resultant solid was isolated by centrifugation and washed with water for three times and ethanol twice. To remove the unreacted BDC, the as-synthesized sample was washed with

DMF twice and soaked in methanol for three days at 60 °C, during which methanol was replaced daily. Finally, the product was dried overnight at 60 °C under vacuum.

S4.3. Synthesis of hcp-UiO-66(Hf)-NaI

NaI (300 mg, 2 mmol) was dissolved in 4 mL deionized water, and then AA (0.85 mL, 15 mmol) was added. The mixture was stirred to form a homogeneous solution. Subsequently, HfCl₄ (192 mg, 0.6 mmol) and BDC (83 mg, 0.5 mmol) were added into the above mixture. Then, the mixture was heated to 90 °C for 24 h under static condition. The resultant solid was isolated by centrifugation and washed with water for three times and ethanol twice. The follow-up procedure is the same as that for UiO-66(Zr)-NaI.

S4.4. Synthesis of UiO-66(Hf)-Arg

L-arginine (840 mg, 4.8 mmol) was dissolved in 3.3 mL deionized water with 1 mL HCl (37%), HfCl₄ (192 mg, 0.6 mmol) and BDC (100 mg, 0.6 mmol) were added into the above mixture. After stirring for 1 min at room temperature, the mixture was heated to 90 °C for 24 h under static condition. The resultant solid was isolated by centrifugation and washed with water for three times and ethanol twice. The follow-up procedure is the same as that for UiO-66(Zr)-NaI.

S4.5. Synthesis of UiO-66(Ce)

NaClO₄·H₂O (84 mg, 0.6 mmol) was dissolved in 1.2 mL deionized water. Subsequently, (NH₄)₂Ce(NO₃)₆ (110 mg, 0.2 mmol) and BDC (33 mg, 0.2 mmol) were added into the above mixture. After stirring for 6 h at room temperature, the resultant solid was isolated by centrifugation and washed with water for three times and ethanol twice. To remove the unreacted BDC, the as-synthesized sample was washed with DMF twice and soaked in methanol for three days at 60 °C, during which time the methanol was changed every day. Finally, the product was dried overnight at 60 °C under vacuum.

S4.6. Synthesis of MIL-53(Al)-X

When NaNO₃, NaI, NaClO₄ and GdmCl were used as the mediators, the molar composition of the reagents was 1AlCl₃·6H₂O: 0.5BDC: 5X: 846H₂O, where X = NaNO₃, NaI, NaClO₄ and GdmCl.

In a typical synthesis, the MIL-53(Al)-X was prepared as following.

NaI (750 mg, 5 mmol) was dissolved in 15 mL deionized water. The mixture was stirred to form a homogeneous solution. Subsequently, AlCl₃·6H₂O (241 mg, 1 mmol) and BDC (83 mg, 0.5 mmol) were added into the above mixture. Then, the mixture was heated to 100 °C for 24 h under static condition. The resultant solid was isolated by centrifugation and washed with water for three times and ethanol twice. To remove the unreacted BDC, the as-synthesized sample was washed with DMF twice and soaked in methanol for two days at 60 °C, during which time the methanol was changed every day. Finally, the product was dried overnight at 60 °C under vacuum.

S4.7. Synthesis of MIL-101(Cr)-NaI

When NaI was used as the mediator, the molar composition of the reagents was 1Cr(NO₃)₃·9H₂O: 1BDC: xNaI: 4230H₂O. To investigate the optimum synthesis conditions of MIL-101(Cr)-NaI, the feed ratio of NaI to BDC was varied from 0 to 30 (x=0-30).

In a typical synthesis, the MIL-101(Cr)-NaI was prepared as following.

NaI (1000 mg, 6.67 mmol) was dissolved in 20 mL deionized water. Subsequently, Cr(NO₃)₃·9H₂O (133 mg, 0.33 mmol) and BDC (55 mg, 0.33 mmol) were added into the above mixture. Then, the mixture was heated to 120 °C for 72 h under static conditions. The resultant solid was isolated by centrifugation and washed with water for three times and ethanol twice. To remove the unreacted BDC, the as-synthesized sample was washed with DMF twice and soaked in methanol for two days at 60 °C, during which time the

methanol was changed every day. Finally, the product was dried overnight at 60 °C under vacuum.

S4.8. Synthesis of MIL-101(Cr)-Gdm

When GdmCl was used as the mediator, the molar composition of the reagents was $1\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$: 1BDC: $x\text{GdmCl}$: $2256\text{H}_2\text{O}$. To investigate the optimum synthesis conditions of MIL-101(Cr)-Gdm, the feed ratio of Gdm to BDC was varied from 0 to 20 ($x=0-20$).

In a typical synthesis, the MIL-101(Cr)-Gdm was prepared as following.

GdmCl (950 mg, 10 mmol) was dissolved in 40 mL deionized water. Subsequently, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (400 mg, 1 mmol) and BDC (166 mg, 1 mmol) were added into above mixture. Then, the mixture was heated to 120 °C for 96 h under static conditions. The resultant solid was isolated by centrifugation and washed with water for three times and ethanol twice. The follow-up procedure is the same as that for MIL-101(Cr)-NaI.

S4.9. Synthesis of UiO-66(Zr) derivatives

The molar composition of the reagents was $1\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$: 1BDC-X: 3NaI: 21AA: $338\text{H}_2\text{O}$, where X= -NH₂, -NO₂, -OH, -COOH, -CH₃, -Br. The mixture was heated to 90 °C for 12 h under static condition. The resultant solid was isolated by centrifugation and washed with water for three times and ethanol twice. The follow-up procedure is the same as that for UiO-66(Zr)-NaI.

S4.10. Synthesis of UiO-66(Ce) derivatives

$\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (84 mg, 0.6 mmol) was dissolved in 1.2 mL deionized water. Subsequently, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ (110 mg, 0.2 mmol) and BDC-X (X=-NO₂, -CH₃, -Br) (0.2 mmol) were added into the above mixture. After stirring for 5 min at room temperature, the resultant solid was isolated by centrifugation and washed with water for three times and ethanol

twice. To remove the unreacted ligands, the as-synthesized sample was washed with DMF twice and soaked in methanol for two days at 60 °C, during which methanol was replaced daily. Finally, the product was dried overnight at 60 °C under vacuum.

S4.11. Large-scale synthesis of UiO-66(Ce) derivatives

NaClO₄·H₂O (8.4 g, 60 mmol) was dissolved in 120 mL deionized water. Subsequently, (NH₄)₂Ce(NO₃)₆ (11 g, 20 mmol) and BDC-X (X=-NO₂, -CH₃, -Br) (20 mmol) were added into the above mixture. After stirring for 5 min at room temperature, the resultant solid was isolated by centrifugation and washed with water for three times and ethanol twice. To remove the unreacted ligands, the as-synthesized sample was soaked in DMF for 4 h then soaked in methanol for two days at 60 °C, during which methanol was replaced daily. Finally, the product was dried overnight at 60 °C under vacuum.

S4.12. Synthesis of MIL-I01(Cr)-NH₂

GdmCl (475 mg, 5 mmol) was dissolved in 10 mL deionized water. Subsequently, Cr(NO₃)₃·9H₂O (400 mg, 1 mmol) and BDC-NH₂ (181 mg, 1 mmol) were added into above mixture. Then, the mixture was heated to 120 °C for 24 h under static conditions. The resultant solid was isolated by centrifugation and washed with water for three times and ethanol twice. The follow-up procedure is the same as that for MIL-I01(Cr)-NaI.

S5. Results and Discussion

S5.1. The optimization of synthesis conditions for hcp-UiO-66(Zr)

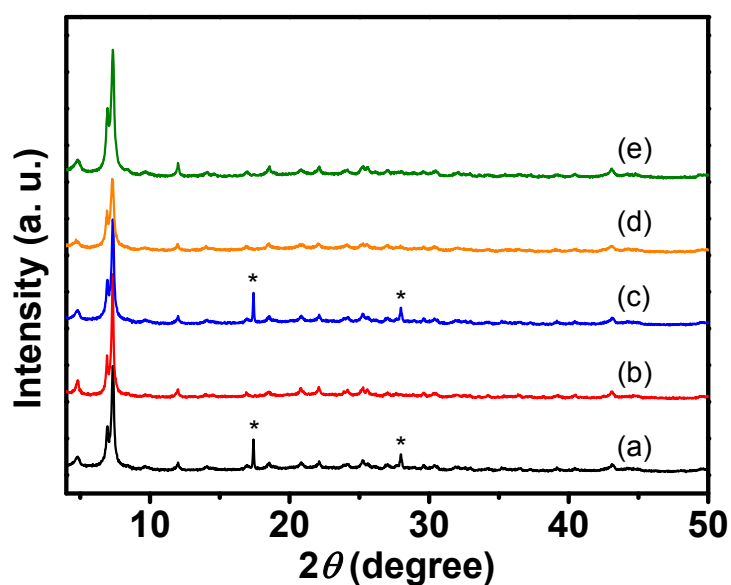


Figure S4. XRD patterns for the hcp-UiO-66(Zr) MOFs synthesized with various salting-in species. The molar composition of the reagents was $1\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O} : 0.75\text{BDC} : 3\text{X} : 17\text{AA} : 338\text{H}_2\text{O}$, where $\text{X} = \text{NaNO}_3$ (a), NaI (b), NaClO_4 (c), NaSCN (d) and GdmCl (e). Asterisks indicate the reflections attributed to the H₂BDC phase.

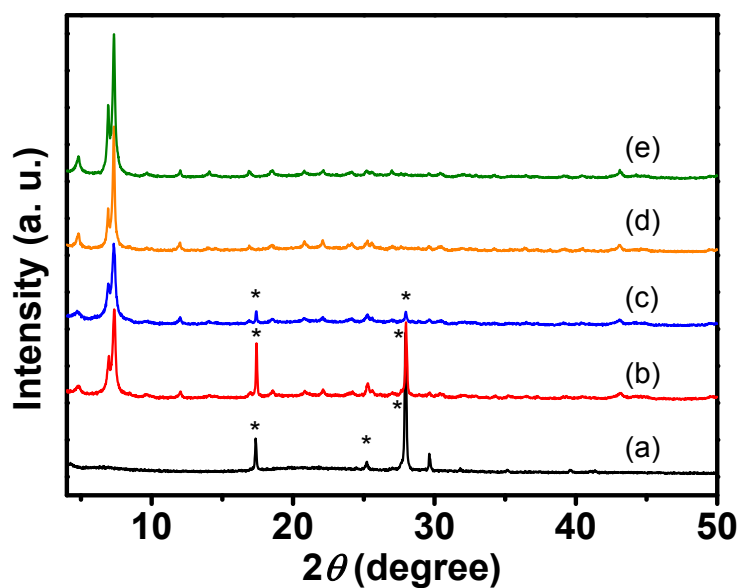


Figure S5. XRD patterns for the hcp-UiO-66(Zr) MOFs synthesized with NaI. The feed ratios of NaI to Zr was $x:1$ with (a) $x = 0$, (b) $x = 0.5$, (c) $x = 1$, (d) $x = 3$, (e) $x = 6$. The final molar composition of the reaction mixture was $1\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O} : 0.75\text{BDC} : x\text{NaI} : 17\text{AA} : 338\text{H}_2\text{O}$. Asterisks indicate the reflections attributed to the H_2BDC phase.

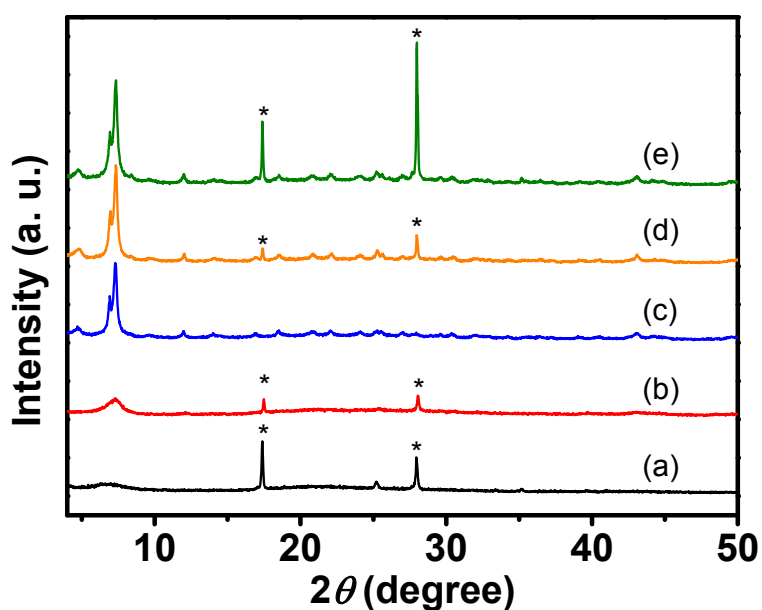


Figure S6. XRD patterns for the NaI promoted hcp-UiO-66(Zr) MOFs synthesized with different amount of AA. The feed ratios of acetic acid to Zr was $x:1$ with (a) $x = 0$, (b) $x = 9$,

(c) $x = 17$, (d) $x = 20$, (e) $x = 24$. The final molar composition of the reaction mixture was $1\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O} : 0.75\text{BDC} : 3\text{NaI} : x\text{AA} : 338\text{H}_2\text{O}$. Asterisks indicate the reflections attributed to the H_2BDC phase.

S5.2. Characterization of the UiO-66(Zr)

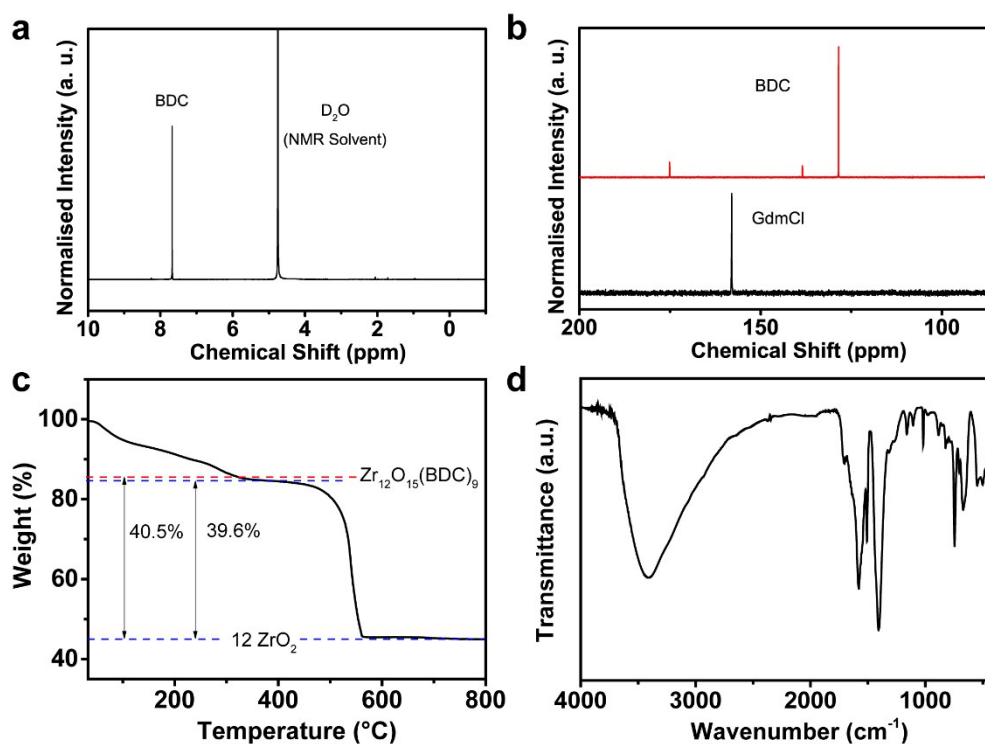


Figure S7. Characterization of the hcp-UiO-66(Zr). a, ^1H NMR spectrum of digested hcp-UiO-66(Zr)-NaI. b, ^{13}C NMR spectrums of GdmCl (black) and digested hcp-UiO-66(Zr)-Gdm (red). c, TGA profile for the hcp-UiO-66(Zr)-NaI. Assuming the residue is pure ZrO_2 , and considering the theoretical composition of dehydroxylated defect-free hcp-UiO-66(Zr)-NaI is $\text{Zr}_{12}\text{O}_{15}(\text{BDC})_9$. The red dashed line represents the position of the theoretical TGA plateau of the defect-free $\text{Zr}_{12}\text{O}_{15}(\text{BDC})_9$ (=85.5%). d, FT-IR spectrum of the hcp-UiO-66(Zr)-NaI.

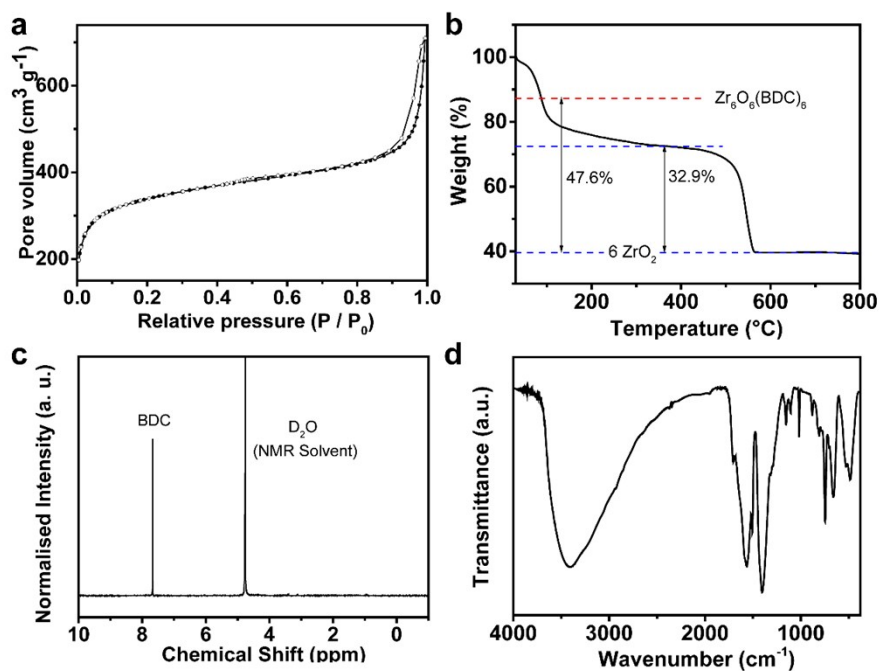


Figure S8. Characterization of the UiO-66(Zr)-Arg. a) N₂ sorption isotherm for the UiO-66(Zr)-Arg. S_{BET} is determined to be 1286 m² g⁻¹. b) TGA profile for the UiO-66(Zr)-Arg. Assuming the residue is pure ZrO₂, and considering the theoretical composition of dehydroxylated defect-free UiO-66(Zr)-Arg is Zr₆O₆(BDC)₆. The red dashed line represents the position of the theoretical TGA plateau of the defect-free Zr₆O₆(BDC)₆ (=87.2%). c) ¹H NMR spectrum of digested UiO-66(Zr)-Arg after extraction. d) FT-IR spectrum of the UiO-66(Zr)-Arg.

S5.3. Characterization of the UiO-66(Hf) MOFs

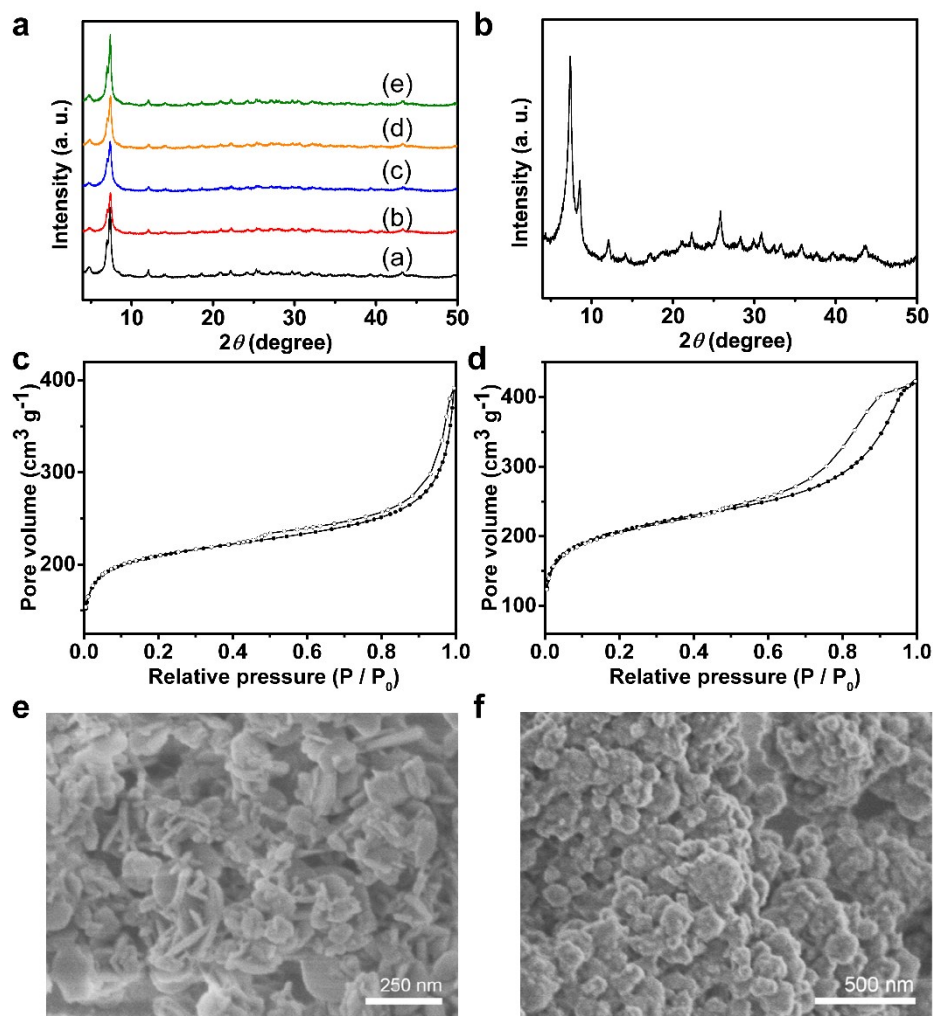


Figure S9. a) XRD patterns for the hcp-UiO-66(Hf) MOFs synthesized with (a) NaI, (b) NaNO₃, (c) NaClO₄, (d) NaSCN and (d) GdmCl. b) XRD patterns for the UiO-66(Hf) MOFs synthesized with L-arginine. c, d, N₂ sorption isotherms for the (c) hcp-UiO-66(Hf)-NaI and (d) UiO-66(Hf)-Arg. The isotherms are a hybrid type I and type IV, which demonstrating its mesoporous characteristics. The mesopores may come from the interstitial voids between the nanosheets. S_{BET} is determined to be 805 m² g⁻¹ and 765 m² g⁻¹, respectively. e), f) Typical SEM images of hcp-UiO-66(Hf)-NaI (e) and UiO-66(Hf)-Arg (f).

S5.4. Characterization of the UiO-66(Ce)

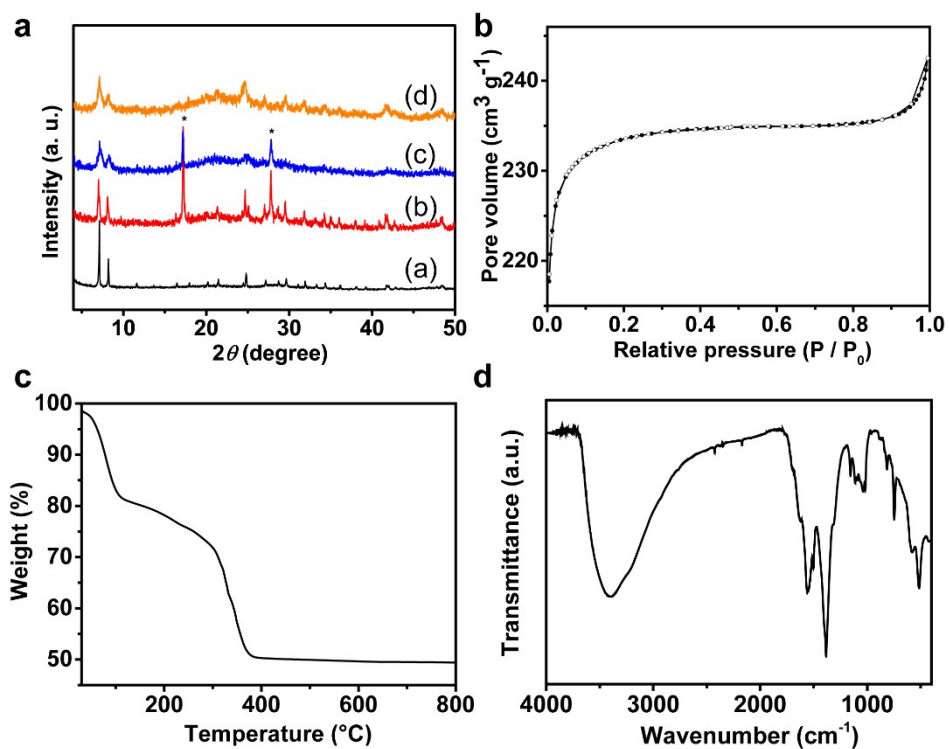


Figure S10. a) XRD pattern for the UiO-66(Ce) synthesized with (a) NaClO₄, (b) NaNO₃, (c) GdmCl and (d) L-arginine. Asterisks indicate the reflections attributed to the H₂BDC phase. b) N₂ sorption isotherm for the UiO-66(Ce). S_{BET} is determined to be 968 m² g⁻¹. c) TGA profile for the UiO-66(Ce). d) FT-IR spectrum of the UiO-66(Ce).

S5.5. Characterization of the MIL-53(Al)

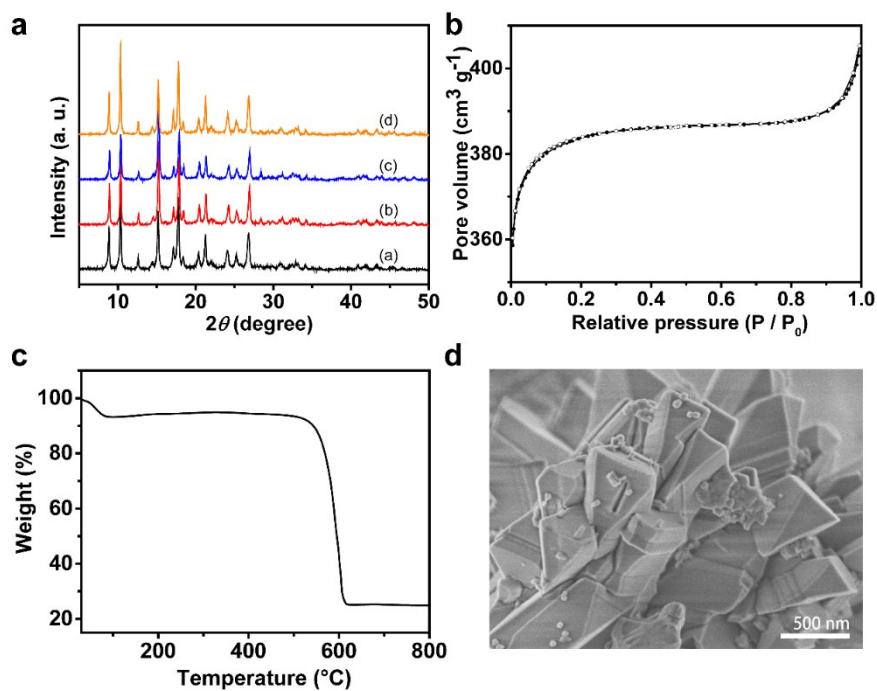


Figure S11. a) XRD patterns for the as-synthesized MIL-53(Al) MOFs synthesized with (a) NaNO_3 , (b) NaI , (c) NaClO_4 and (d) GdmCl . b) N_2 sorption isotherm for the MIL-53(Al) synthesized with NaI . S_{BET} is determined to be $1564 \text{ m}^2 \text{ g}^{-1}$. c) TGA profile for the MIL-53(Al)_{sol} synthesized with NaI . d) A typical SEM image of the as-synthesized MIL-53(Al).

S5.6. Characterization of the MIL-101(Cr)

S5.6.1 The optimization of synthesis conditions for MIL-101(Cr)

In the case of MIL-101(Cr)-NaI, the NaI/BDC ratio significantly affected the crystallinity of the product. When the NaI/BDC ratio was lower than 10, no diffraction peaks of crystalline phase were detectable (Figure S12a). When the NaI/BDC ratio was set up to 10, the broad characteristic diffraction peaks of MIL-101 began to appear, SEM image shows that the product is made up of aggregated nanoparticles of approximately 20 nm in size (Figure S12b and S13a). N₂ sorption isotherms exhibit type I isotherms with BET surface area of only 1635 m² g⁻¹ (Figure S14 and Table S1). Further increasing the amount of the NaI, the widths of diffraction peaks became smaller, which indicated the formation of larger crystals (Figure S12c-e). The SEM pictures of samples show a development from intergrown aggregates of nanoparticles to individual spherical particles with increasing size (Figure S13b-d). The N₂ sorption isotherms began to exhibit the characteristic steps of the MIL-101 structure with the higher specific BET surface area over 2000 m² g⁻¹ (Figure S14 and Table S1). The optimal crystallinity of the MIL-101(Cr) could be obtained with the NaI/BDC feed ratios around 20 to 23. The crystallinity weakened somewhat as the amounts of the applied NaI were either greater or smaller than that ratios.

When using GdmCl as a mediator, the effect was different from that of NaI. The feed amount of Gdm was more likely to affect the reaction time. When the Gdm/BDC ratio was lower than 5, no product could be obtained. When 5-9 equivalents of Gdm were introduced, though MIL-101(Cr) could be obtained with satisfactory crystallinity, the reaction time need to be prolonged to over a week. However, the reaction time could be shortened to 96 hours by adding ten equivalents GdmCl, but with the further increase of Gdm, the reaction time did not change significantly. Therefore, for the sake of time efficiency, the minimum feed ratio of Gdm/BDC was determined to be 10.

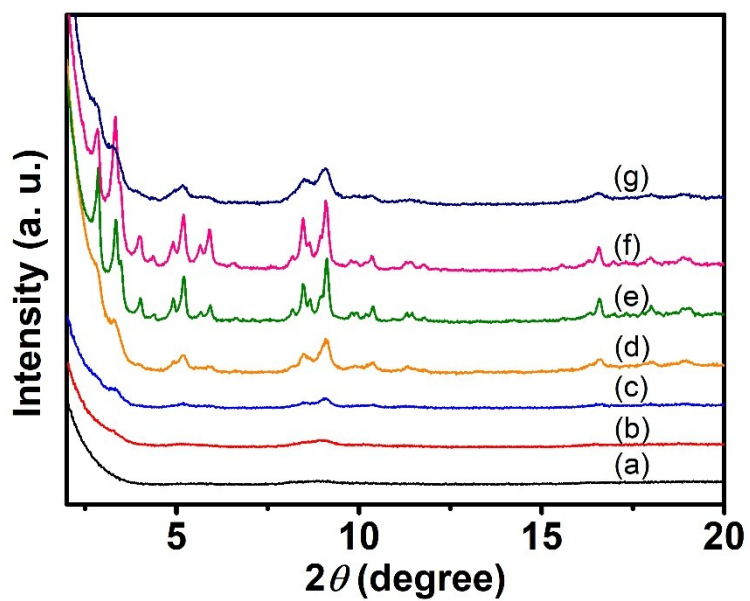


Figure S12. XRD patterns for the MIL-101(Cr) MOFs synthesized with NaI. The feed ratios of NaI to BDC was $x:1$ with (a) $x = 5$, (b) $x = 10$, (c) $x = 15$, (d) $x = 18$, (e) $x = 20$, (f) $x = 23$ and (g) $x=30$.

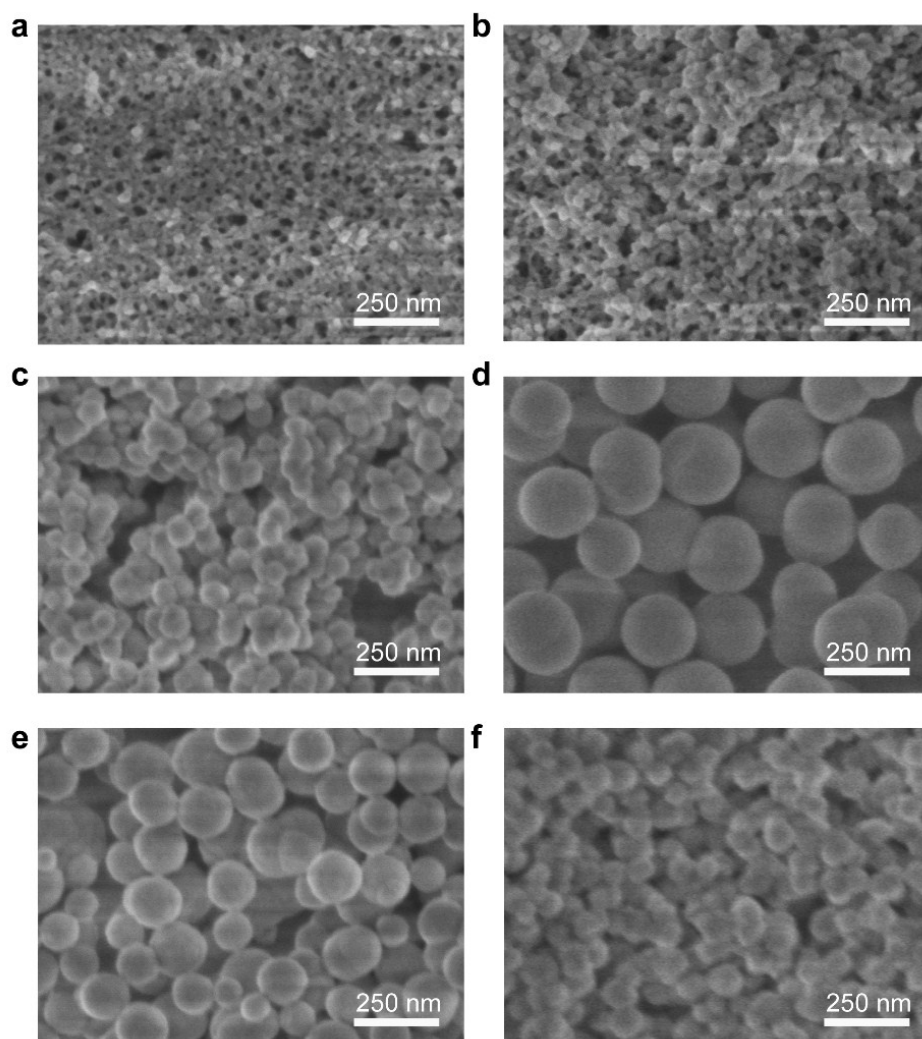


Figure S13. Typical SEM images of the MIL-101(Cr) synthesized with NaI. The feed ratios of NaI to BDC was $x:1$ with (a) $x = 10$, (b) $x = 15$, (c) $x = 18$, (d) $x = 20$, (e) $x = 23$ and (f) $x = 30$.

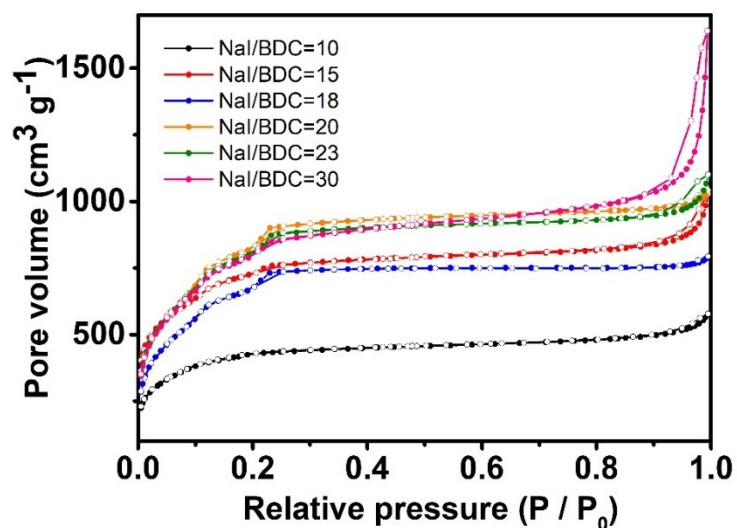


Figure S14. N₂ sorption isotherms for the MIL-101(Cr) synthesized with different feed ratios of NaI to BDC.

Table RC1. Textural parameters for the MIL-101(Cr) synthesized with different feed ratios of NaI to BDC.

Samples	S _{BET} (m ² /g)	V _P (cm ³ /g)
NaI/BDC=10	1635	0.89
NaI/BDC=15	2265	1.23
NaI/BDC=18	2777	1.43
NaI/BDC=20	3314	1.70
NaI/BDC=23	3220	1.54
NaI/BDC=30	2940	1.61

S5.6.2 Characterization of the MIL-101(Cr)-Gdm

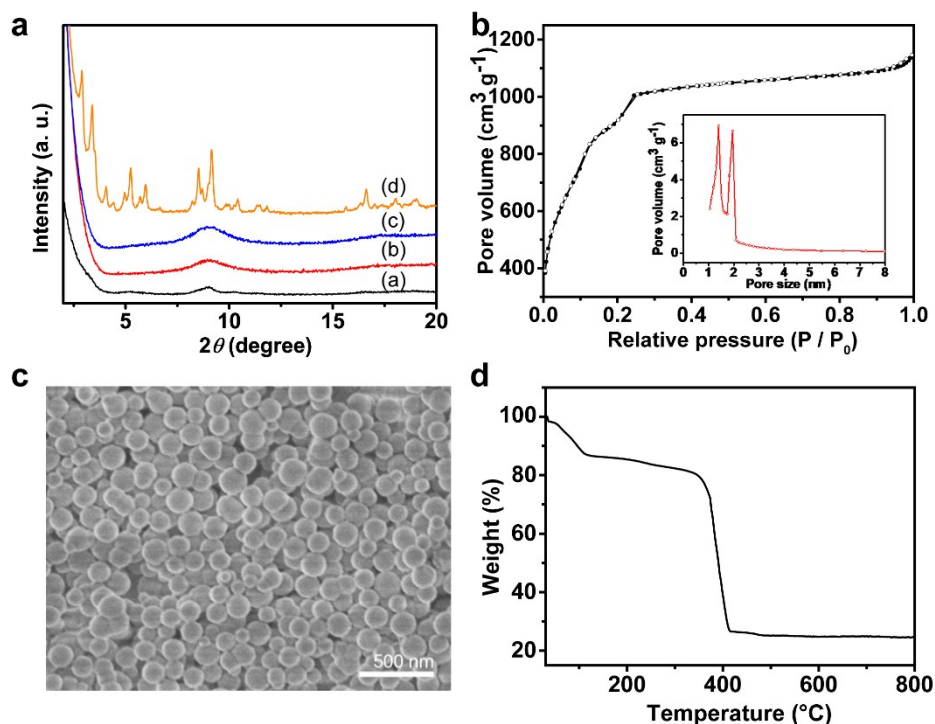


Figure S15. a) XRD pattern for the MIL-101(Cr) synthesized with GdmCl. b) N₂ sorption isotherm for the MIL-101(Cr) synthesized with GdmCl. S_{BET} is determined to be 3243 m² g⁻¹. The pore size distribution profile calculated by BJH equation points out two monodispersed pores peaking at about 14.0 and 19.5 Å (inset). c) A typical SEM image of the MIL-101(Cr) synthesized with GdmCl. d) TGA profile for the MIL-101(Cr) synthesized with NaI.

S5.7. Characterization of MOFs synthesized with functionalized BDC ligands.

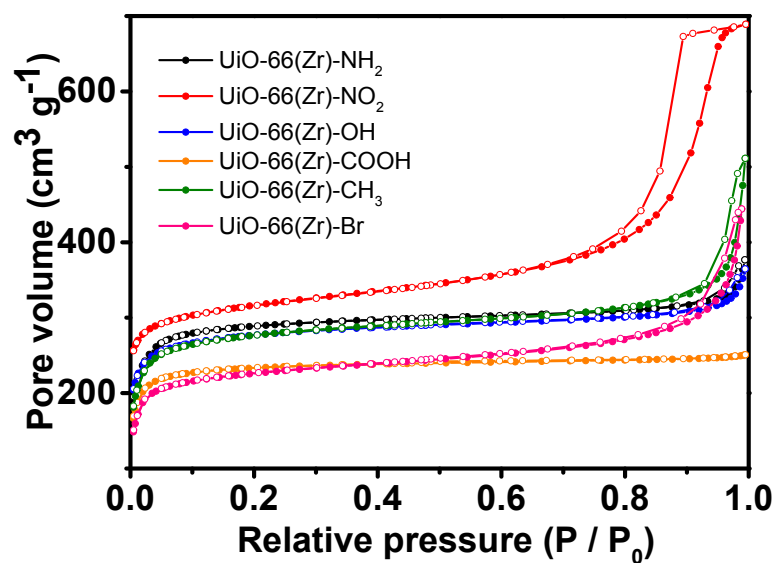


Figure S16. N₂ sorption isotherms for the UiO-66(Zr) derivatives synthesized with NaI.

Table S2. Textural parameters for the UiO-66(Zr) derivatives synthesized with NaI.

Samples	S _{BET} (m ² /g)	V _P (cm ³ /g)
UiO-66(Zr)-NH ₂	1132	0.58
UiO-66(Zr)-NO ₂	810	0.68
UiO-66(Zr)-OH	1064	0.56
UiO-66(Zr)-COOH	928	0.39
UiO-66(Zr)-CH ₃	1067	0.79
UiO-66(Zr)-Br	883	0.68

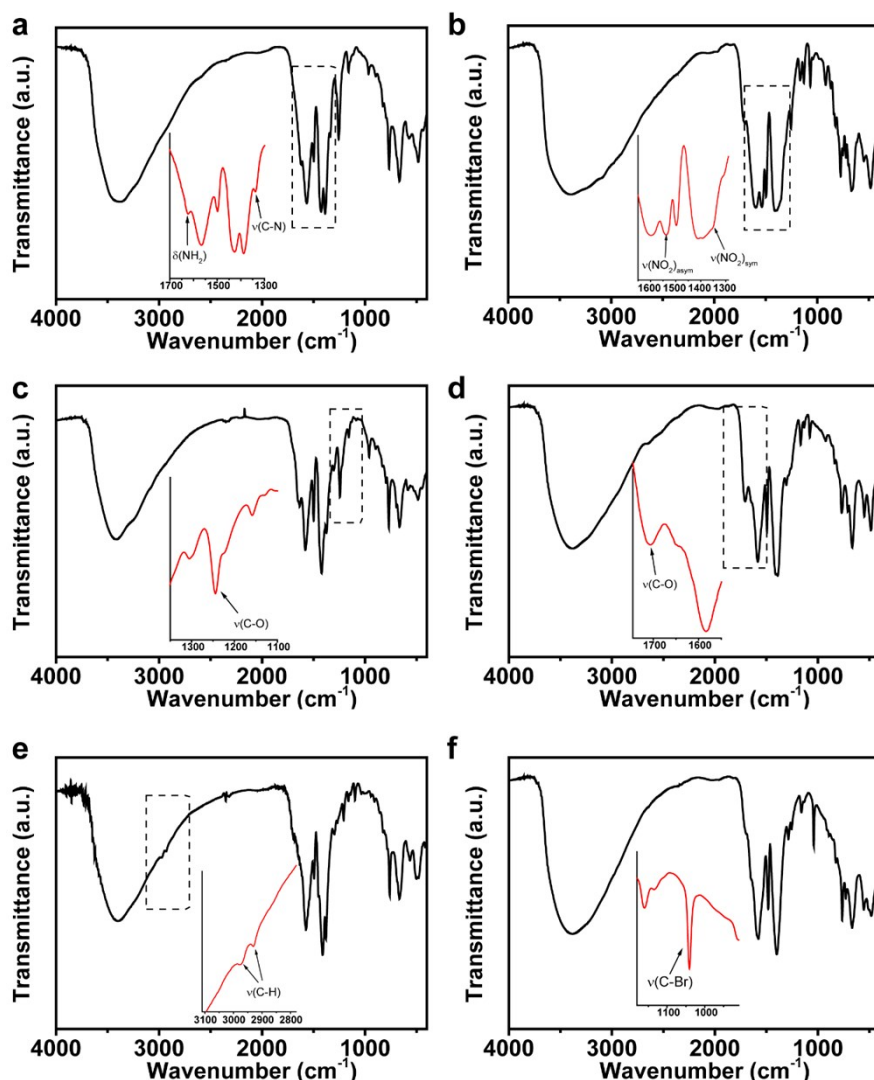


Figure S17. FT-IR spectra of the UiO-66(Zr) derivatives. a) UiO-66(Zr)-NH₂. The arrows indicate the N-H bending (scissoring) vibration of amino group at 1624 cm⁻¹ and C-N stretching of aromatic amines at 1336 cm⁻¹. b) UiO-66(Zr)-NO₂. The arrows indicate the characteristic nitro group asymmetric ($\nu(\text{NO}_2)_{\text{asym}}$) and symmetric ($\nu(\text{NO}_2)_{\text{sym}}$) stretching vibrations at 1536 cm⁻¹ and 1352 cm⁻¹, respectively. c) UiO-66(Zr)-OH. The arrows indicate the characteristic C-O stretching vibration of hydroxyl group at 1244 cm⁻¹. d) UiO-66(Zr)-COOH. The arrows indicate the characteristic C-O stretching vibration of -COOH at 1705 cm⁻¹. e) UiO-66(Zr)-CH₃. The arrows indicate the characteristic C-H stretching vibrations at 2926 cm⁻¹ and 2973 cm⁻¹. f) UiO-66(Zr)-Br. The arrows indicate the characteristic C-Br stretching vibration at 1039 cm⁻¹.

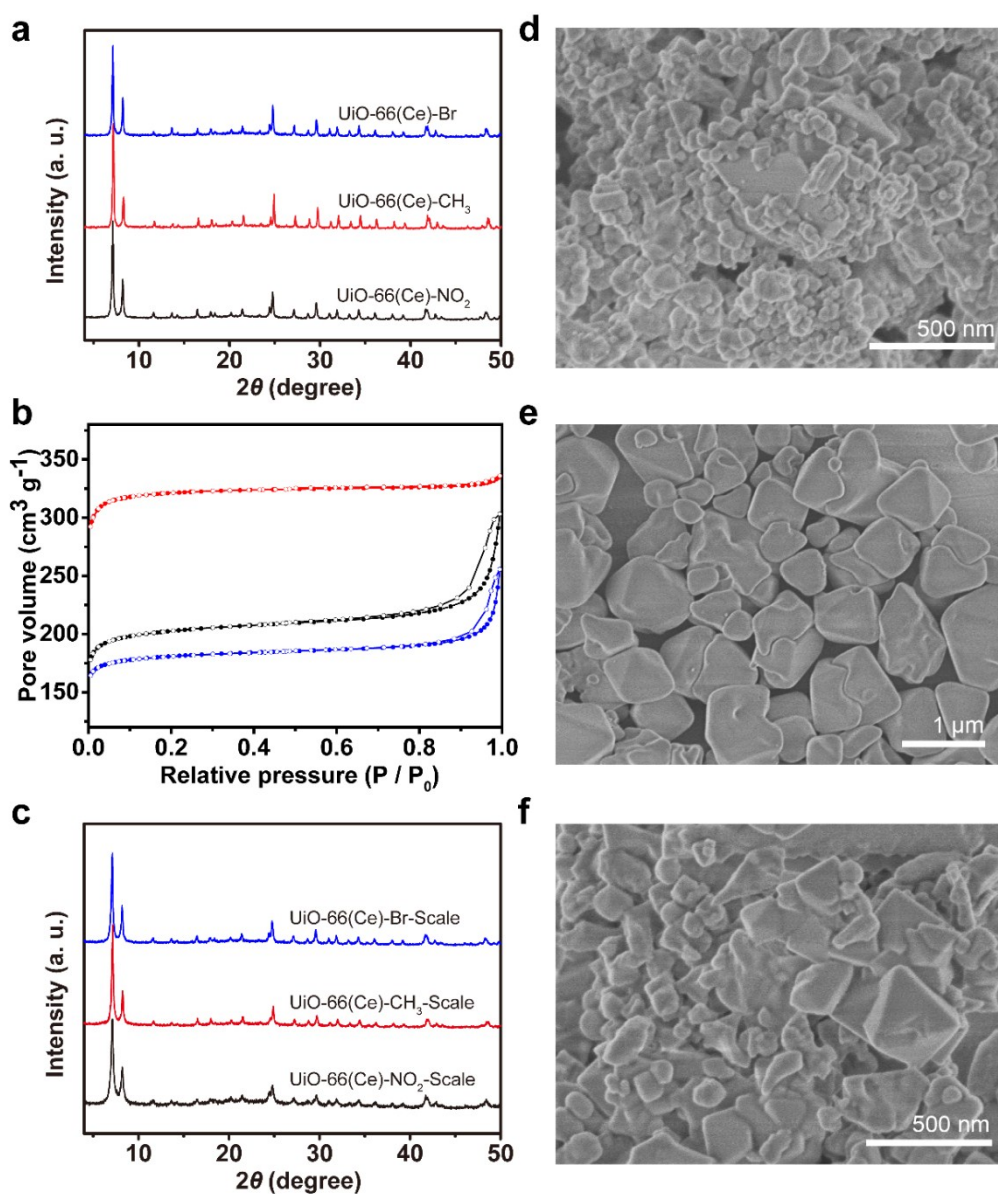


Figure S18. Characterization of UiO-66(Ce) derivatives. a) XRD patterns of UiO-66(Ce) derivatives synthesized at room temperature. b) N₂ sorption isotherm for the UiO-66(Ce)-NO₂ (black), UiO-66(Ce)-CH₃ (red) and UiO-66(Ce)-Br (blue). c) XRD patterns for the large-scale synthesized UiO-66(Ce) derivatives. d), e), f) Typical SEM images of the UiO-66(Ce)-NO₂ (d), UiO-66(Ce)-CH₃ (e) and UiO-66(Ce)-Br (f).

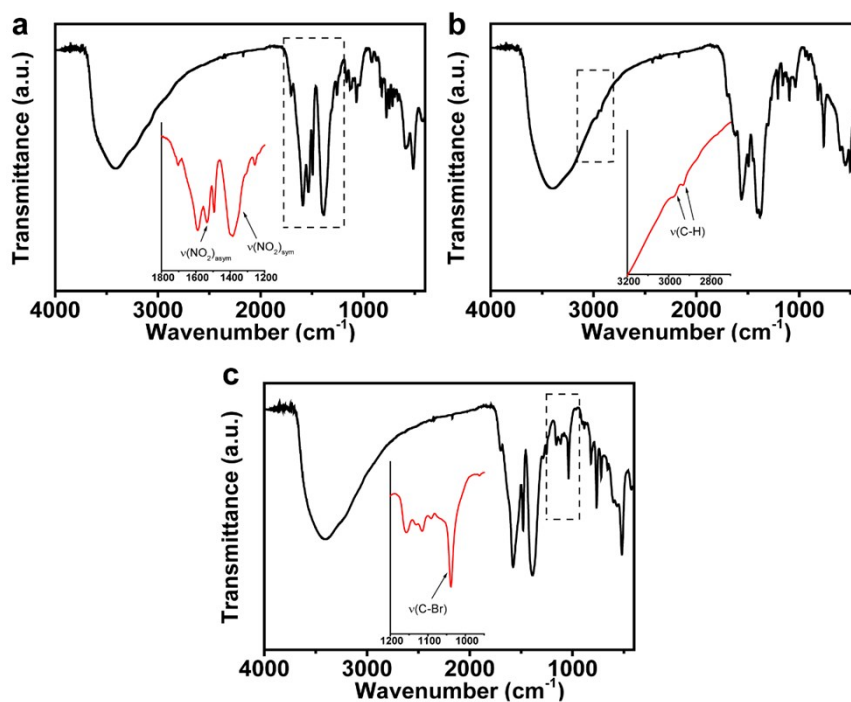


Figure S19. FT-IR spectra of the UiO-66(Ce) derivatives. a) UiO-66(Ce)-NO₂. The arrows indicate the characteristic nitro group asymmetric ($\nu(\text{NO}_2)_{\text{asym}}$) and symmetric ($\nu(\text{NO}_2)_{\text{sym}}$) stretching vibrations at 1532 cm⁻¹ and 1345 cm⁻¹, respectively. b) UiO-66(Ce)-CH₃. The arrows indicate the characteristic C-H stretching vibrations at 2926 cm⁻¹ and 2974 cm⁻¹. c) UiO-66(Ce)-Br. The arrows indicate the characteristic C-Br stretching vibration at 1038 cm⁻¹.

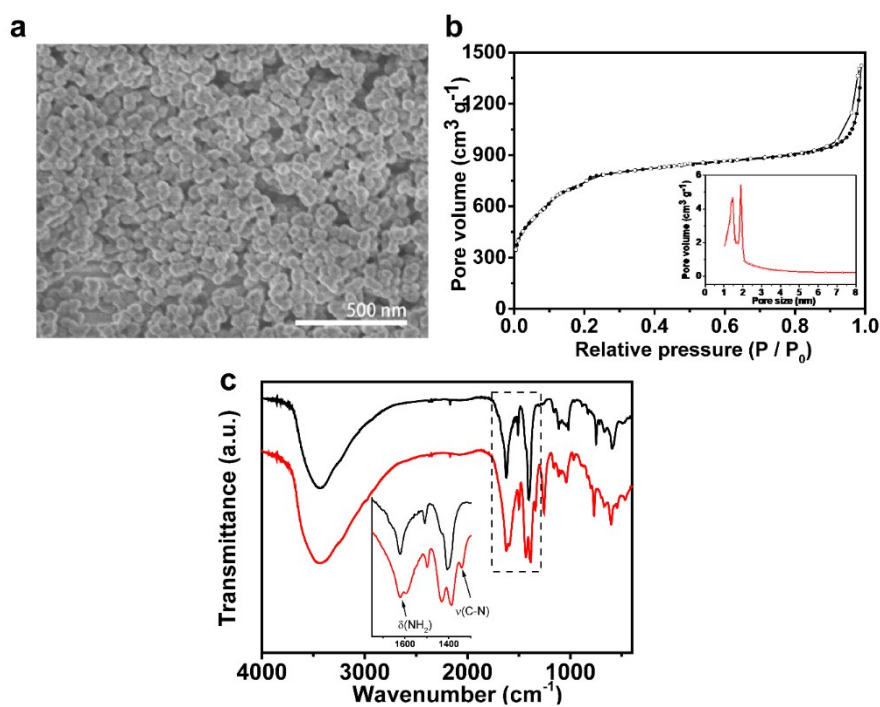


Figure S20. Characterization of MIL-101-NH₂. a) A typical SEM image of the MIL-101(Cr)-NH₂ synthesized with GdmCl. b) N₂ sorption isotherm for the MIL-101(Cr) synthesized with GdmCl. S_{BET} is determined to be 2947 m² g⁻¹. The pore size distribution profile calculated by BJH equation points out two monodispersed pores peaking at about 14.7 and 18.9 Å (inset). c) Comparison of FT-IR spectra of MIL-101 (black) and MIL-101-NH₂ (red). The arrows indicate the N-H bending (scissoring) vibration of amino group at 1622 cm⁻¹ and C-N stretching of aromatic amines at 1337 cm⁻¹.